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(54) Title: HYDROGENATION OF SUBSTRATE AND PRODUCTS MANUFACTURED ACCORDING TO THE PROCESS

(57) Abstract

A typical traditional reactor for hydrogenation consists of a tank filled with a liquid and a gas and a small particle catalyst. The reaction is carried out at high pressures and high temperatures. Lack of gas on the catalyst surface limits the velocity of reaction. Much work has been done to increase the quantity of gas on the catalyst. It has not been possible to solve this problem effectively with the techniques of today. According to the invention an extra solvent is added to the reaction mixture. By bringing the whole mixture (solvent, substrate, hydrogen and reaction products) to super-critical or near-critical state, a substantially homogeneous mixture can be obtained. By this method it is possible to control the concentration of gas on the catalyst to the desired level. The velocity of reaction is thereby increased considerably. The hydrogenation reactions principally involved comprise hydrogenation of carbon-carbon double bonds (C=C) in lipids; hydrogenation of COOR to C-OH and HO-R to produce fatty alcohols; and direct hydrogenation of oxygen to hydrogen peroxide.

HYDROGENATION OF SUBSTRATE AND PRODUCTS MANUFACTURED ACCORDING TO THE PROCESS

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TECHNICAL FIELD OF THE INVENTION.

The present invention relates to a process for the hydro-genation of a substrate, where hydrogen gas is mixed with the substrate in the presence of a catalyst and the reaction
10   is carried out at certain reaction conditions of pressure, time and temperature. The hydrogenation reactions are mainly related to the hydrogenation of carbon–carbon double bonds (C=C) in lipids;
hydrogenation of COOR to C–OH and HO–R for the manufacturing of fatty alcohols; and the direct hydrogenation of oxygen to hydrogen peroxide.

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BACKGROUND OF INVENTION.

C=C in lipids.
The annual production of vegetable oils is about 90 million tons (Mielke 1992), of
20   which about 20% are hardened (hydrogenated). Furthermore, about 2 million tons of marine oils are hydrogenated yearly. The production is spread over the whole industrialized world. Through the hydrogenation, hydrogen is added to the double bonds of the unsaturated fatty acids. The largest part of the oils is only partly hydrogenated. The desired conditions of melting and the desired consistency of the fats are thereby
25   obtained, which are of importance for the production of margarine and shortening. The tendency to oxidation is reduced by the hydrogenation, and the stability of the fats is increased at the same time (Swern 1982).

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In the future, the lipids may be modified by methods belonging to bio technology, especially gene technology, but hydrogenation will certainly remain.

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A problem with the hydrogenation processes of today is, that new fatty acids are produced which to a great extent do not exist in the nature. They are often called bans fatty acids, but the double bonds change position as well as form (cis–trans) during the hydrogenation (Allen 1956, Allen 1986).

As a rule, bans fatty acids are desired from a technical and functional point of view (Swern 1982), but regarding health, their role is becoming more and more questionable (Wahle & James 1993).

A typical state of the art reactor for hydrogenation is a large tank (5 to 20 m) filled with oil and hydrogen gas plus a catalyst in the form of fine particles (nickel in powdery form). The reaction is carried out at a low pressure, just above atmospheric (0,5 to 5 bar), and high temperatures (130 to 210°C). The hydrogen gas is thoroughly mixed into the oil, as this step restricts the velocity of the reaction rate (Grau et al., 1988).

If the pressure of hydrogen gas is increased from 3 to 50 bar when soya oil is partially hydrogenated (iodine number at the start = 135, at the end = 70), the content of bans is reduced from 40 to 15 %. The position isomerization is also reduced to a corresponding level (Hsu et al., 1989). These results are of no commercial interest, as these conditions enforce a replacement of the low pressure autoclaves by high pressure autoclaves.

According to the "half hydrogenation" theory, the con–centration of activated H–atoms on the catalyst surface determines the number of double bonds being hydrogenated and deactivated without being hydrogenared respectively. A lack of activated H–atoms causes a transand position– isomerization (Allen 1956, Allen 1986). A lack of activated H–atoms can be the consequence of low solubility of H2 in the oil, or of a bad catalyst (poisoned or inadequately produced). Thus, the "half hydrogenation" theory corresponds very well to the empirical results (Allen 1956; Allen 1986; Hsu et al., 1989).

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It is possible to deodorize and hydrogenate an oil in the presence of CO_2 and hydrogen (Zosel 1976). Zosel describes in detail how to use CO_2 in order to deodorize the oil. However, it must be emphasized that Zosel does not give any hint, that CO_2 should have an influence on the hydrogenation process. Furthermore, Zosel does not touch on

5   the cis/trans problem.

In the experiments of Zosel, the catalyst is surrounded by an liquid phase during the entire process. Zosel does not disclose the composition, but in the light of the other data, we estimate that the liquid phase consists of oil (about 95%), CO_2 (about 5%)

10   and hydrogen (about 0,03%). This phase is far away from a super critical condition. As a consequence, the velocity of reaction is limited by the concentration of hydrogen on the catalyst surface. The same applies to all traditional hydrogenation reactions where the catalyst is in the liquid phase as well. The velocity of hydrogenation in the experiments of Zosel is about 100 kg/m3h, i.e. somewhat lower than in traditional

15   hydrogenizing reactors.

FATTY ALCOHOLS.

Fatty alcohols and their derivatives are used in shampoo, detergent compositions and

20   cosmetic preparations etc. The annual production is about 1 million tons. About 60% is based on petrochemicals, and about 40% is derived from natural fats and oils. The raw material for short chain fatty alcohols, C12–C14, is coco–nut oil and palm kern oil, whereas C16–C18 comes from tallow, palm oil or palm stearin (Kreutzer 1984, Ong et al.,1989).

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It is theoretically possible to hydrogenate triglycerides, fatty acids and methyl esters to fatty alcohols. A direct hydrogenation of triglycerides has not been developed commercially, because the glycerol will be hydrogenated as well and thus lost. A direct hydrogenation of fatty acids requires corrosion resistant materials and a catalyst resistant

30   to acids (Kreutzer 1984). Lurgi has developed a hydrogenation process (the slurry process), where fatty acids are introduced and are quickly esterified with a fatty alcohol

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to a wax ester, and then the wax ester is hydrogenated (copper chromite, 285°C, 300
bar)(Buchhold 1983, Voeste Buchhold 1984, Lurgi 1994).

Most plants for the production of natural fatty alcohols are based on methyl esters as
raw material. Saturated fatty alcohols are produced at a temperature of about 210°C and
a pressure of 300 bar using copper chromite as catalyst in a fixed bed reactor. Other
catalysts as copper carbonate, nickel or copper and chromic oxide will also function
(Mahadevan 1978, Monick 1979, Lurgi 1994). Unsaturated fatty alcohols are produced
at about 300°C and 300 bar, normally using zinc chromite as catalyst. There are also
other catalysts which selectively hydrogenate the group COOR, leaving the C=C
unimpaired (Klonowski et al., 1970; Kreutzer 1984).

The reaction is limited by the solubility of hydrogen in the liquid (Hoffman Ruthhardt
1993).

Davy Process Technology markets a gas phase process where methyl esters are
hydrogenated to fatty alcohols (40 bar, 200 to 250°C, catalyst without chromium)
(Hi].es 1994).

A lot of work has been done to develop catalysts functioning with less energy (lower
temperature, lower pressure). Another object has been to develop methods for a direct
hydrogenation of triglycerides to fatty alcohols without a simultaneous hydrogenation
of the glycerol (Hoffman Ruthhardt 1993).

HYDROGEN PEROXIDE.

Hydrogen peroxide is used in large quantities for bleaching, cleaning, as a disinfectant
and as a raw material in industrial processes etc. Earlier, hydrogen peroxide was derived
by an electrolytic process. Now, oxidation of substituted hydroquinone or 2–propanol
is most widely used.

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There are a lot of patents concerned with direct synthesis of hydrogen peroxide from oxygen and hydrogen. The reaction medium can be acidic organic solvents or water with organic solvents using noble metals, most often palladium, as catalyst (EP-B-0049806; EP-B-0117306; US-A-4336239; EP-B-0049809).

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It is preferred that the reaction medium is free from organic constituents because of problems with purification. Several patents use acidic water as the reaction medium (pH = 1-2) with addition of halides, especially bromide and chloride (<1 mM) and with noble metals or mixtures of noble metals as catalysts (EP-A-0132294; EP-A-0274830;

10   US-A-4393038; DE-B-2655920; DE 4127918 A1).

The velocities of reaction which are disclosed are about 1 kg/m3h, and the selectivity (mol hydrogen peroxide/mol hydrogen reacted) is about 75% (DE 4127918 A1).

15   According to theory, one can expect to obtain high selectivity with high concentrations of oxygen and hydrogen on the catalyst surface (Olivera et al., 1994).

THE OBJECT OF THE INVENTION AND MOST IMPORTANT CHARACTERISTICS.

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The object of the present invention is to obtain a very effective process for partial or complete hydrogenation of the substrates mentioned above.

According to the invention, this problem has been solved by mixing the substrate,

25   hydrogen gas and solvent, and by bringing the whole mixture in to a super-critical or near-critical state. This substantially homogeneous super-critical or near-critical solution is led over the catalyst, whereby the reaction products formed, i.e. the hydrogenated substrates, will also be a part of the substantially homogeneous super-critical or near-critical solution.

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The solvent can be a saturated hydrocarbon or an unsaturated hydrocarbon which on hydrogenation gives a saturated hydrocarbon, e.g. ethane, ethene, propane, propene, butane, butene, or CO_2, dimethyl ether, "freons", N_2O, N_2, NH_3, or mixtures thereof.

5   Propane is a suitable solvent for many lipids. CO_2 is a suitable solvent for hydrogen peroxide and water.

The catalyst will be selected according to the reaction which is to be carried out. For a partial or complete hydrogenation of only C=C bonds, preferably a noble metal or
10   nickel will be selected. For a selective hydrogenation of COOR to C-OH and HO-R, the catalyst would preferably be a zinc salt, e.g. zinc chromite. For a simultaneous hydrogenation of COOR to C-OH and HO-R and a hydrogenation of C=C, the preferred catalyst would be copper chromite, another salt of copper or copper free from chrome. For a partial hydrogenation of oxygen to hydrogen peroxide, the
15   preferred catalyst would be a noble metal.

According to the invention, the conceration of hydrogen on the catalyst surface can be controlled to very high levels. The proportion of bans fatty acids in partially hydrogenated fatty products will be much lower according to the invention than by
20   using conventional processes, where the product has been hydrogenated to the same level using the same catalyst. The hydrogenated products will preferably contain less than 10% bans fatty acids.

DESCRIPTION OF THE DRAWINGS.

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Figure 1 is a diagram showing the percentage of bans fatty acids as a function of the degree of hydrogenation according to a traditional technique and according to the invention. Figure 2 is a flow sheet for a process according to the invention.

30   DESCRIPTION OF THE INVENTION.

The problem. In a great number of hydrogenation processes, hydrogen gas is mixed with a liquid substrate and a fixed catalyst, e.g. in the hydrogenation of lipids. In certain cases the substrate can be a gas and the product a liquid, e.g. hydrogenation of oxygen to hydrogen peroxide and water. In both these cases, the velocity of reaction is limited

5   by the concentration of gas on the catalyst surface. The reason is the transport resistances of the gas: between the gas phase and the liquid phase; through the liquid phase; and between the liquid phase and the catalyst.

THE SUBJECT MATTER OF THE INVENTION.

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The idea is to add a solvent, which completely dissolves the gas as well as the liquid, resulting in a substantially homogeneous mixture of hydrogen, substrate, product and solvent. This is possible, if the whole mixture is in a super-critical or near-critical state. The defition substantially homogeneous means, that the principal part of

15   the gas is in the continuous phase which covers the catalyst surface. One method to confirm this is to observe the velocity of reaction, which increases dramatically when the continuous phase that covers the catalyst surface is substantially homogeneous.

VELOCITY OF REACTION.

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According to the invention, the following transport resistances of the gas are reduced substantially: gas phase/liquid phase; through the liquid phase; and liquid phase/catalyst. The velocity of reaction thereby increases to a very high degree; from about 10 to about 1000 times. The consequence of this is that continuous reactors will be preferred

25   compared to the batch reactors of to-day. The selectivity is also influenced to a very high degree.

SOLVENT.

30   In order to bring the whole mixture (hydrogen, substrate, product and solvent) to super-critical or near-critical state at appropriate pressures and temperatures, the solvent must dissolve substrate and product as much as possible.

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Glycerides, fatty acids and many derivatives of fatty acids are completely miscible with super-critical propane (Peter et al.,1993). Propane can be used in any proportions together with food according to EU-regulations (Sanders 1993; EC 1984). Thus, propane is a very adequate solvent in reactions with lipids.

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Water dissolves to a certain extent in CO2 (King et al., 1992). Hydrogen peroxide dissolves more easily than water in CO2. Thus, CO2 is an appropriate solvent for direct synthesis of hydrogen peroxide. (For a thorough description of super-critical technology, see McHugh Krakonis 1986; Dohrn 1994).

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CATALYSTS.

The catalysts which are used today in traditional
processes can in principle also be used in super-critical processes. The catalyst may however be modified to optimize selectivity, velocity of reaction, length of life, filtering properties and pressure-drop.

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QUALITY OF PRODUCT.

20   The invention, enables new possibilities to control the hydrogen concentration at the catalyst. The velocity of reaction increases substantially. The selectivity can also be influenced in certain processes. By partial hydrogenation of edible oils, the content of bans fatty acids is of importance for the quality (see background of invention).

25   Figure 1 illustrates in principle how the proportion of bans fatty acids changes during hydrogenation with two different catalysts, one catalyst according to a traditional technique and another according to the new super-critical technique. The new super-critical technique makes it possible to reduce the content of bans fatty acids in comparison with the traditional technique using the same catalyst and the same degree

30   of hydrogenation. However, using different catalysts, the difference may be less.

In Figure 1, "trad" means traditional process; and "sf" means process with super critical fluid. "cat" means catalyst.

CONDITIONS OF REACTION.

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C=C in lipids.

I. Partial hydrogenation. At partial hydrogenation, the reaction is interrupted at a certain iodine number, e.g. 60. The substrate, e.g. vegetable, animal or marine oil, and hydrogene are dissolved in a solvent, e.g. propane. The mixture is brought to a super-

10   critical or a near-critical state. The substantially homogeneous mixture is brought into contact with a catalyst, e.g. palladium. The content of trans fatty acids in the final product is less than 10%. The optimal reaktion condition may occure over a wide experimental range and this range can be described as follows:

15

–temperature	0 – 250°C	20 – 200°C
–pressure	10 – 350 bar	20 – 200 bar
–time of reaction	0* – 10 min	1 usec– 1 min
–solvent	30 – 99, 9wt%	40 – 99wt%

20   The solvent must dissolve the substrates at the concentrations used. The solvent can be ethane, ethene, propane, propene, butane, butene, CO_2, dimethyl ether, "freons", N_2O, N_2, NH_3 or mixtures of these gases. Preferred are propane, propene, butane, butene and dimethyl ether. Most preferred is propane.

25   –concentration of H_2 0* – 3wt% 0,001 – 1wt%

–concentr. substrate   0,1   – 70wt% 1 – 60wt%

–type of substrate C=C in general; glycerides are preferred

(mono-, di-, triglycerides, galactolipids, phospholipids), also fatty acids or their derivatives (e.g. methyl- and ethyl-esters).

30   –catalysts noble metals: Pd, Pt, Os, but also Ni. (O* means

very low values, below the lowest one under "preferably").

II. COMPLETE HYDROGENATION.

At complete hydrogenation, all double bonds are hydrogenated and the iodine number
is therefore near zero. The substrate, e.g. vegetable, animal or marine oil, and hydrogen
are dissolved in a solvent, e.g. propane. The mixture is brought to a supercritical or
near-critical condition, and the substantially homogeneous mixture is brought into
contact with a catalyst, e.g. palladium.

The optimal conditions of reaction are wide and can be described in a similar way as
for partial hydrogenation; the temperature is, however, somewhat higher than for partial
hydrogenation (T is probably higher than Tkrit).

FATTY ALCOHOLS.

The substrate, e.g. the triglyceride, the fatty acid or its
derivative, and hydrogen are mixed together with a solvent,
e.g. propane. The mixture is brought to a super-critical or
a near-critical state, and the substantially homogeneous mixture is brought into contact
with a catalyst. Different groups can be hydrogenated depending on the catalyst used
(see below under "-catalyst").

The optimal reaction condition may occure over a wide experimental range and this
range can be described as follows:

	in general	preferably
-temperature	20 - 300°C	40 - 300°C
-pressure	10 - 350 bar	20 - 200 bar
-time of reaction	0* - 10 min	1μsec- 1 min
-solvent	30 - 99,9wt%	40 - 99wt%

The solvent must dissolve the substrates at the concentrations used. The solvent can be
ethane, ethene, propane, propene, butane, butene, CO2, dimethyl ether, "freons", N2O,
N2, NH3 or mixtures of these gases. Preferred are propane, propene, butane, butene,

and dimethyl ether. Sometimes, it can be advantageous to use an entrainer. Most preferred is pure propane.

5	−concentration H2	0* − 3wt%	0,001 − 1wt%
	−concentr. substrate	0,1 − 70wt%	1 − 60 wt%
	−type of substrate:	COOR in general. Preferred are fatty acids and their derivatives (e.g. methyl−ethyl− or wax esters), and also mono− di−, and tri−glycerides, but also galac− tolipids and phospholipids.	
10	−catalyst	a)selective hydrogenation of COOR, but not C=C or C−OH, e.g. zinc chromite or	

another salt of zinc.

b) hydrogenation of both COOR and C=C

but not C−OH, e.g. copper chromite or

copper free from chrome or an other salt of copper.

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(0* means very low values, less than the lowest under "preferably").

An example of suitable values at optimal conditions is: substrate 10 wt%, propane about 90 wt%, hydrogen 0,2 wt%; the mixture is brought into contact with a bed of
20   catalyst at 250°C and 150 bar, and has an average contact time of 30 sec.

HYDROGEN PEROXIDE.

Oxygen and hydrogen are mixed in a solvent, e.g. CO_2. The mixture is brought to a
25   super−critical or near−critical state, and the substantially homogeneous mixture is brought in contact with a catalyst. The solvent dissolves the reaction products, hydrogen peroxide and water. Thus, a substantially homogeneous mixture is maintained in the reactor.

30   The optimal reaction condition may occure over a wide experimental range and this range can be described as follows:

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	in general	preferably
–temperature	10 – 200°C	20 – 10 0 ° C
–pressure	10 – 350 bar	30 – 300 bar
–time of reaction	0* – 10 min	1μsec– 1 min
–solvent	10 – 99, 9wt%	60 – 99wt%

The solvent must dissolve water and hydrogen peroxide at the concentrations used. The solvent can be CO_2, N_2, NH_3, or mixtures of these gases. It may also be advantageous to use an entrainer. Pure CO_2 is probably the most suitable solvent.

–concentration H2	0* – 10wt%	0,1 – 3wt%
–concentration O2	0,1 – 80wt%	1 – 30wt%

–catalyst   noble metals, e.g. Pd or mixtures of noble metals,
e.g. Pd + Au

–reaction aids   halides, e.g. bromides or chlorides; these can be
added in the process or at the preparation of the catalyst (O* means very low values,
less than the lowest under "preferably")

The risk of explosion during some of the processing steps must be warned against.

Suitable proportions of the added constituents can be exemplified by: oxygen 3wt%, hydrogen O,lwt% and CO_2 96,9wt%. The mixture is brought into contact with a catalyst of palladium at 35°C and 200 bar; the average contact time is 0,1 sec.

EQUIPMENT AND ANALYTICAL METHODS

Equipement

A flow sheet for the continuous reactor used, is illustrated in Figure 2. In this figure "M" is a mixer, "Temp." a temperature controller, "A" a sampling device for analyses, "P" a pressure reduction valve, "Sep" a vessel for separation of gas/liquids and "F" a gasflow–meter. At room temperature a condensed gas, a non–condensable gas and a

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liquid were mixed according to the principles used by Pickel in a "Supercritical Fluid Chromatography" application (Pickel 1991). Pickel mixed CO_2 nitrogen and a liquid entrainer. We mixed propane (l), hydrogen (g) and lipids (see M in Figure 2). The same equipment can be used for the hydrogen peroxide experiments but in this case one add:

5   CO_2 (l); oxygen + hydrogen (g); recation acides (l).

The mixture was heated to the desired reaction temperature and was brought into an HPLC tube filled with a catalyst powder (see Temp and Reactor in Figure 2).

10   After the reactor samples were collected from the high pressure section using an HPLC valve (see A in Figure 2 and Härröd et al 1994).

The pressure was reduced to atmospheric pressure and lipids and gases were separated (see P and Sep in Figure 2). The gasflow was controlled by the pressure–reduction

15   valve (P om Figure 2).

Analysis

The product quality was analysed using silver–ion–HPLC and gradient elution (Elfman

20   Härröd 1995). This method is developed from an isocratic method (Adolf 1994). The kind (cis/trans) and the amount of the fatty acid methyl esters (FAME) was determine. From these data the iodine value (IV) was calculated.

The density was calculated from the Peng–Robinsson equation of state (Dohrn 1994).

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EXAMPLES

Example 1

30   Partial hydrogenation of methylesters from rapeseed oil using a palladium catalyst.

Composition and amound of the inlet flow to the reactor:

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	mole%	weight%	mg/min
propane	99.92	99.7	3700
hydrogen	0.04	0.002	0.07
FAME	0.04	0.26	10

Reactio conditions:

catalyst	5% Pd on char coal (E 101 O/D 5% Degussa AG)
reactor volume	0.0007 ml
reaction time	40 ms
temperature	50 °C
pressure	120 bar

productivity and product quality:

productivity   80 000 kg FAME/m^3 h

Iodine-value   reactor inlet=110 reactor outlet=50

FAME with trans   10% of all FAME

Comments

This example shows that a very high productivity (80 000 kg FAME/m^3 h) and a low content of trans-fatty acids (10%) can be attained at near-critical conditions. The results above is only an example. We do not claim that it is the optimal conditions for the process.

Others (Berben et al 1995) has minimized the trans-fatty acid content using the conventional technique. The productivity became much lower (700 kg triglycerides /m^3 h) and the content of the trans-fatty acids became much higher (34%).

Example 2

Complete hydrogenation of methylesters from rapseed oil using a palladium catalyst.

15

Composition and amount of the inlet flow to the reactor:

	mole%	weight%	mg/min
propane	96.27	95.7	1840
hydrogen	3.1	0.14	2.7
FAME	0.63	4.16	80

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Reaction conditions:

catalyst	5% Pd on char coal (E 101 O/D 5% Degussa AG)
reactor volume	0.007
reaction time	80 ms
temperature	90 °C
pressure	70 bar

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15   productivity and product quality:

productivity   700 000 kg FAME/m^3 h

Iodine-value   reactor inlet=110 reactor outlet <1

FAME with trans   <0.1% of all FAME

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Comments

This example shows that a tremendous productivity (700 000 kg FAME/m^3 h) can be attained at near–critical conditions. The results above is only an example. We do not

25   claim that it is the optimal conditions for the process.

Example 3

Complete hydrogenation of methylesters from rapeseed oil using a nickel catalyst.

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Composition and amount of the inlet flow to the reactor:

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	mole%	weight%	mg/min
propane	99.49	99.13	1500
hydrogen	0.38	0.917	0.25
FAME	0.13	0.85	13

Reaction conditions:

catalyst	Nickel (Ni–5256 P, Engelhard)
reactor volume	0.009 ml
reaction time	65 ms
temperature	190 °C
pressure	155 bar

productivity and product quality:

productivity   90 000 kg FAME/m^3 h

Iodine–value   reactor inlet=110 reactor outled <1

FAME with trans   <0.1% of all FAME

Comments

This example shows that a very high productivity (90 000 kg FAME/m^3 h) can be attained using a nickel catalystat super–critical conditions. The results above is only an example. We do not claim that it is the optimal conditions for the process.

Example 4

Complete hydrogenation of triglycerides using a palladium catalyst.

Composition and amount of the inlet flow to the reactor:

	mole%	weight%	mg/min
propane	98.7	93.6	3600
hydrogen	1	0.043	1.6
triglycerides	0.03	6.3	240

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The triglycerides (tg) were in this case a commercial vegetable oil.

Reaction conditions:

    catalyst   5% Pd on char coal (E 101 O/D 5%

5   Degussa AG)

        reactor volume   2.5 ml

        reactor time   12 sec

        temperature   50 °C

        pressure   100 bar

10

productivity and product quality:

        productivity   5000 kg tg/m^3 h

        Iodine-value reactor inlet=140 reactor outlet =0.1

        FA with trans   <0.1% of all FA

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Comments:

This example shows that a high productivity (5000 kg triglycerides/m^3 h) can be attained at near-critical conditions. The results above is only an example. We do not

20   claim that it is the optimal conditions for the process.

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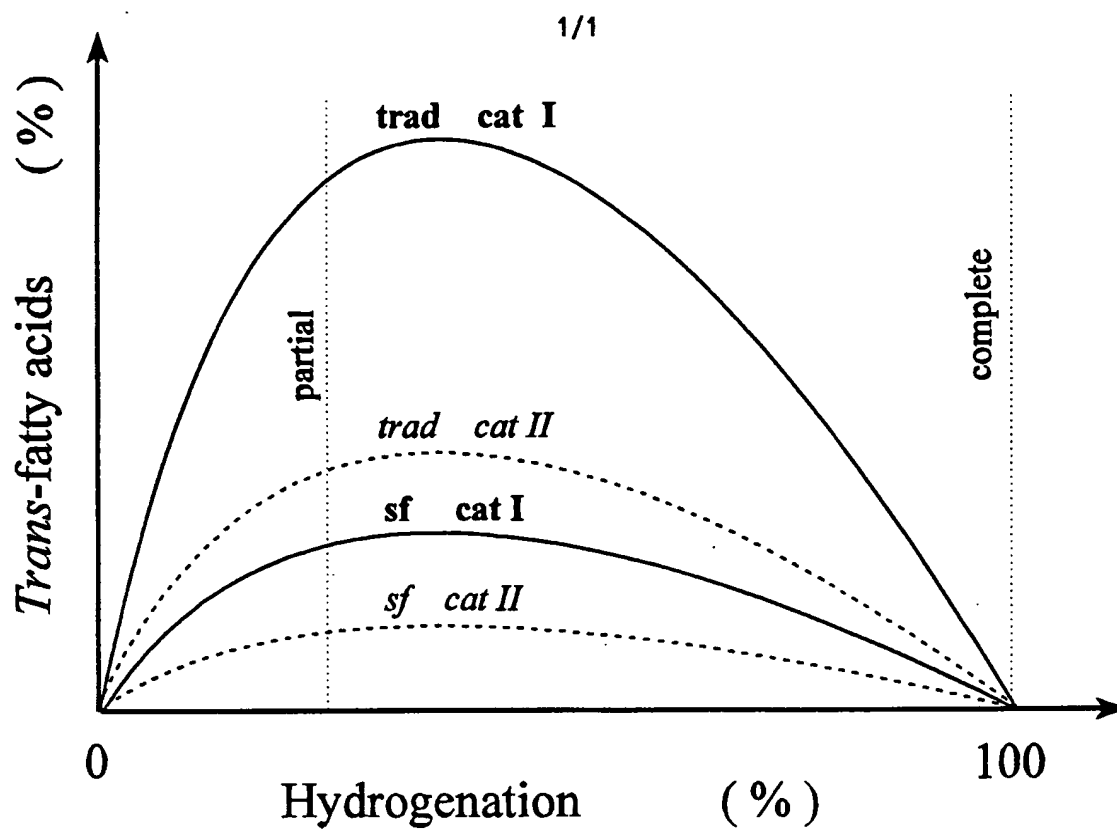
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CLAIMS

1. A process for the hydrogenation of a substrate, where hydrogen gas is mixed with
the substrate in the presence of a catalyst, and the reaction is carried out at selected
conditions of pressure, time and temperature,

c h a r a c t e r i z e d   i n,

that substrate, hydrogen gas and a solvent are mixed together, the mixture is brought
to a super–critical or a near–critical state, and the substantially homogeneous super–
critical or near–critical solution is brought into contact with the catalyst, and also in that
the reaction products, i.e. the hydrogenated substrates, form a constituent in the super–
critical or near–critical solution.

2. A process according to claim 1,

c h a r a c t e r i z e d   i n,

that the substrate comprises lipids such as triglycerides, fatty acids or derivatives of
fatty acids.

3. A process according to either of the preceding claims,

c h a r a c t e r i z e d   i n,

that the solvent comprises a saturated hydrocarbon or an unsaturated hydrocarbon,
which results on hydrogenation in a saturated hydrocarbon, e.g. ethane, ethene, propane,
propene, butane, butene, or CO_2, dimethyl ether, "freons", N_2O, N_2, NH_3, or mixtures
thereof.

4. A process according to claim 3,

c h a r a c t e r i z e d   i n,

that the solvent preferably is propane.

5. A process according to any of the preceding claims,

c h a r a c t e r i z e d   i n,

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that preferably a noble metal or a nickel catalyst is used for the selective hydrogenation of a carbon–carbon–double bond (C=C).

6. A process according to any of the preceding claims,

5   c h a r a c t e r i z e d   i n,

that the reaction is interrupted when the desired iodine number has been obtained, which means an iodine number near zero for full hydrogenation and above zero for partial hydrogenation.

10   7. A process according to any of claims 1, 2, 3 and 4,

c h a r a c t e r i z e d   i n,

that preferably zinc chromite or any other salt of zinc is used as a catalyst for the selective hydrogenation of COOR to C–OH and HO–R.

15   8. A process according to any of claims 1, 2, 3 and 4,

c h a r a c t e r i z e d   i n,

that preferably copper chromite or copper free from chrome, or any other salt of copper is used as a catalyst for the hydrogenation of COOR to C–OH and HO–R and the hydrogenation of C=C.

20

9. A process according to claim 1,

c h a r a c t e r i z e d   i n,

that the substrate comprises oxygen.

25   10. A process according to any of claims 1 and 9,

c h a r a c t e r i z e d   i n,

that the solvent comprises CO2, N2, NH3, or mixtures thereof.

11. A process according to claim 10,

30   c h a r a c t e r i z e d   i n,

that the solvent preferably is CO2.

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12. A process according to any of claims 1, 9, 10 and 11,

c h a r a c t e r i z e d   i n,

that preferably a noble metal is used as catalyst for the hydrogenation of oxygen to

5   hydrogen peroxide.

13. A fatty substance which has been partially hydrogenated according to the process

of any of claims 1 – 6,

c h a r a c t e r i z e d   i n,

10   that it contains a substantially lower part of bans fatty acids, preferably less than 10%

bans fatty acids, than partially hydrogenated fatty products which have been

hydrogenated to the same degree according to conventional processes using a

corresponding catalyst.

15   14. A fatty substance which has been fully hydrogenated according to the process of

any of claims 1 – 6,

c h a r a c t e r i z e d   i n,

that it has been produced according to the process where C=C bonds are hydrogenated

selectively.

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15. A fatty substance which has been hydrogenated according to the process of any of

claims 1, 2 r 3, 4 and 7,

c h a r a c t e r i z e d   i n,

that it has been produced according to the process where COOR is selectively

25   hydrogenated to C–OH and/or HO–R.

16. A fatty substance which has been hydrogenated according to the process of any of

claims 1, 2, 3, 4 and 8,

c h a r a c t e r i z e d   i n,

30   that it has been produced according to the process where COOR is hydrogenated to C–

OH and/or HO–R and C=C also has been hydrogenated.

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17. Hydrogen peroxide which has been partially hydrogenated according to the process
of any of claims 1, 9, 10, 11 and 12,

c h a r a c t e r i z e d   i n,

that it has been produced according to the process where oxygen is hydrogenated.
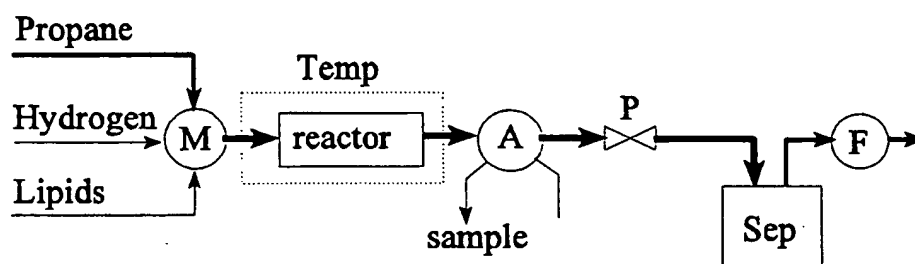
5

Fig 1.

Fig 2.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C11C 3/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C11C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3969382 A (KURT ZOSEL), 13 July 1976 (13.07.76) --	1-17
E	WO 9522591 A1 (DEGUSSA AKTIENGESELLSCHAFT E), 24 August 1995 (24.08.95) -- --------	1-17

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" erlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 October 1995	17 -10- 1995

Name and mailing address of the ISA/	Authorized officer
Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Dagmar Järvman Telephone No. +46 8 782 25 00

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 95/00824

Box I	Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

The wording "substrat", which indicates different products, are to broadly formulated to permit a meanful search. The search on claim 1 has therefore been incomplete. (See Art. 6)

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II	Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest
☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (1)) (July 1992)

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A- 3969382	13/07/76	AT-A,B-	328597	25/03/76
		BE-A,A-	819352	28/02/75
		CA-A-	1031786	23/05/78
		CH-A-	592729	15/11/77
		DE-A-	2441152	06/03/75
		FR-A,B-	2242457	28/03/75
		GB-A-	1481065	27/07/77
		JP-C-	1152770	30/06/83
		JP-A-	50064302	31/05/75
		JP-B-	57022960	15/05/82
		LU-A-	70819	02/01/75
		NL-A-	7411504	04/03/75
		SE-B,C-	407693	09/04/79
		SE-A-	7410974	03/03/75
WO-A1- 9522591	24/08/95	NONE		